

Supporting Information for

Facile Synthesis and Redox Behavior of an Overcrowded Spirogermabifluorene

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1. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **1** and **5** in C_6D_6 .

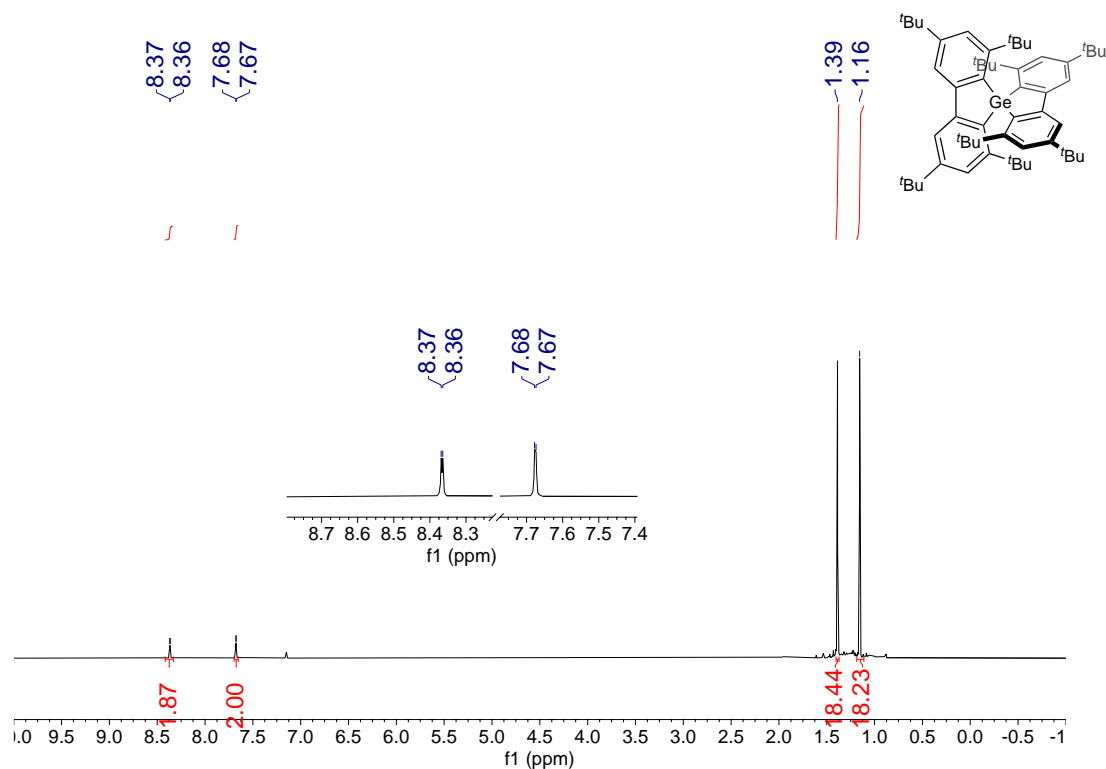


Figure S1. ^1H NMR spectrum of **1** in C_6D_6 .

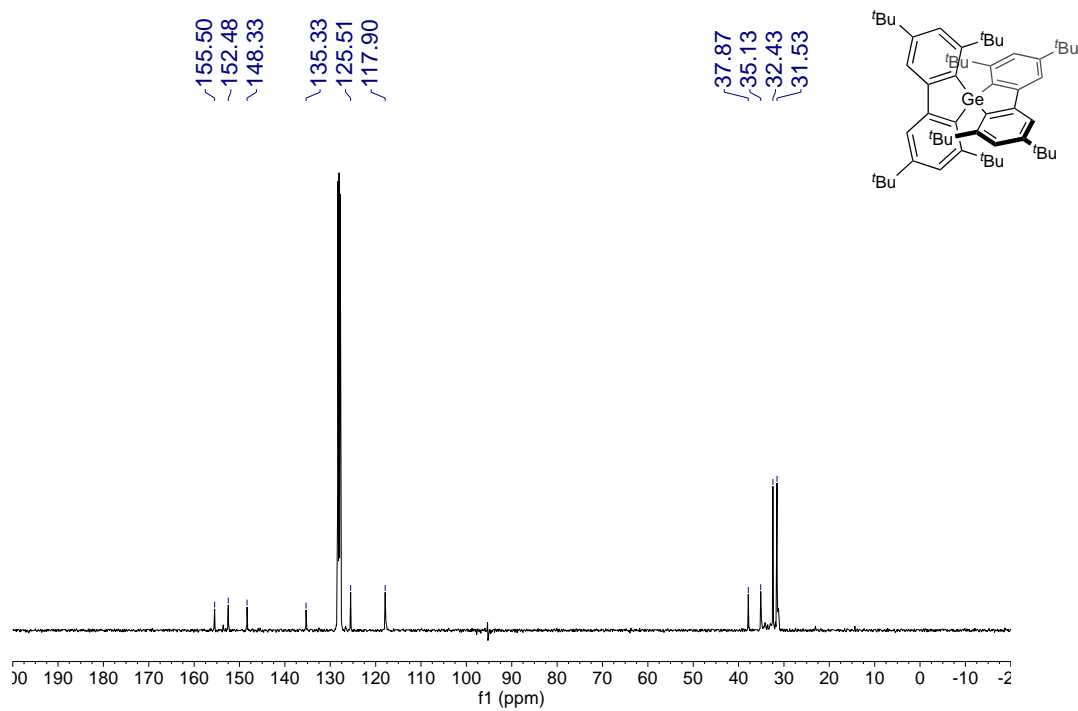


Figure S2. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **1** in C_6D_6 .

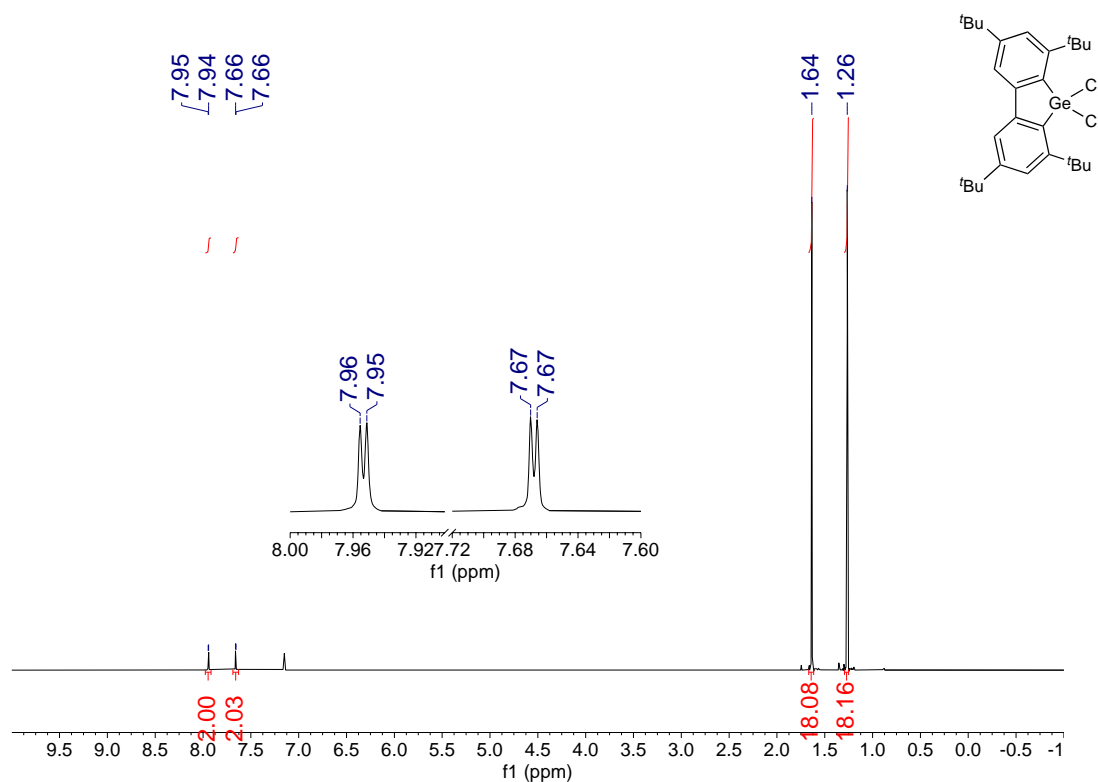


Figure S3. ¹H NMR spectrum of **5** in C₆D₆.

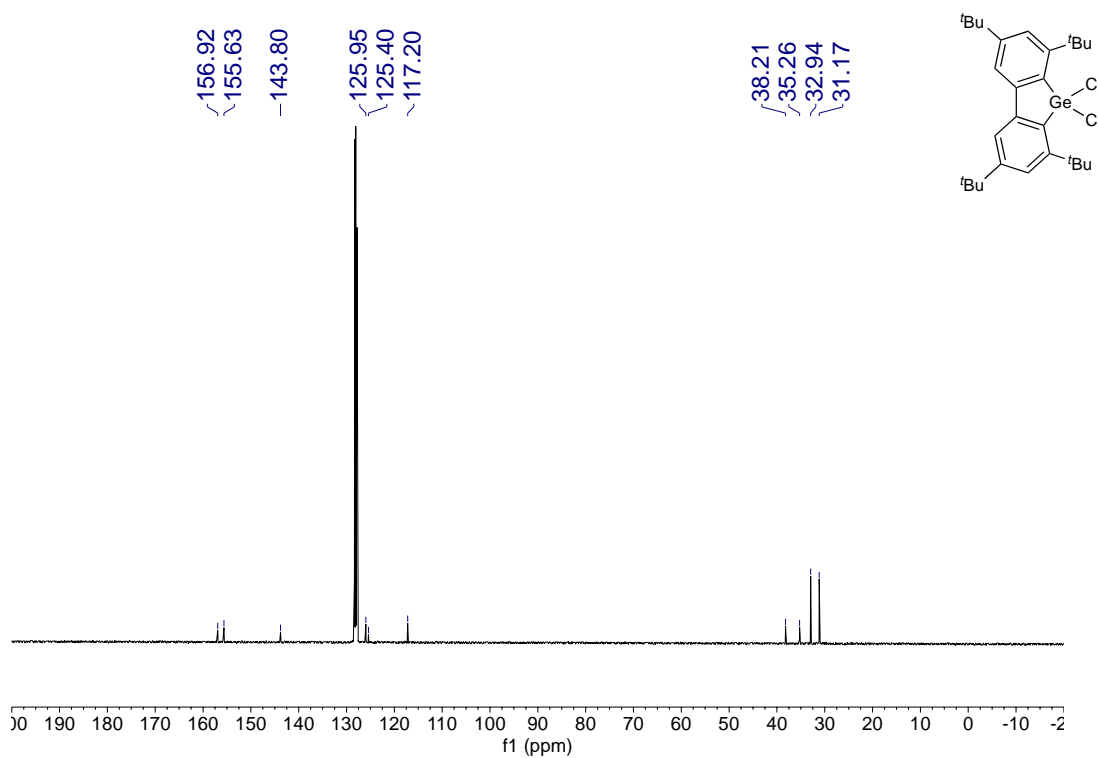


Figure S4. ¹³C{¹H} NMR spectrum of **5** in C₆D₆.

2. Computational calculations for the spirometallabifluorenes and the related species.

All calculations were carried out using the density functional theory (DFT) method with a pure B3PW91-D3(BJ) functional,^[S1,S2] and geometry optimizations and vibrational frequencies were calculated in the gas phase using the 6-311G(2d,p) basis set, as implemented in the Gaussian 16 program package.^[S3] The molecular geometries for the transition states were first estimated using the Reaction plus software package (software to optimize reaction paths along the user's expected ones; HPC Systems Inc., <http://www.hpc.co.jp/chem/react2.html>; written in Japanese), based on the nudged-elastic-band (NEB) method,^[S3] and subsequently re-optimized using the *Gaussian 16* software package.^[S4] Computational time was generously provided by the Supercomputer Laboratory at the Institute for Chemical Research (Kyoto University). The coordinates of the optimized structures are included in the corresponding .xyz files in the Supplementary Materials.

3. UV/vis spectrum for intermediate 6.

The UV/vis spectrum was recorded on a JASCO V-770. The supernatant of the reaction mixture of the *in-situ*-generated **4** and $\text{GeCl}_2 \cdot (\text{dioxane})$ in Et_2O was transferred to a UV-cell under an argon atmosphere at $-80\text{ }^\circ\text{C}$. After the measurement under an argon atmosphere, the solution was exposed to air, and then measured under ambient atmosphere. The obtained differential spectrum is shown in Figure S5.

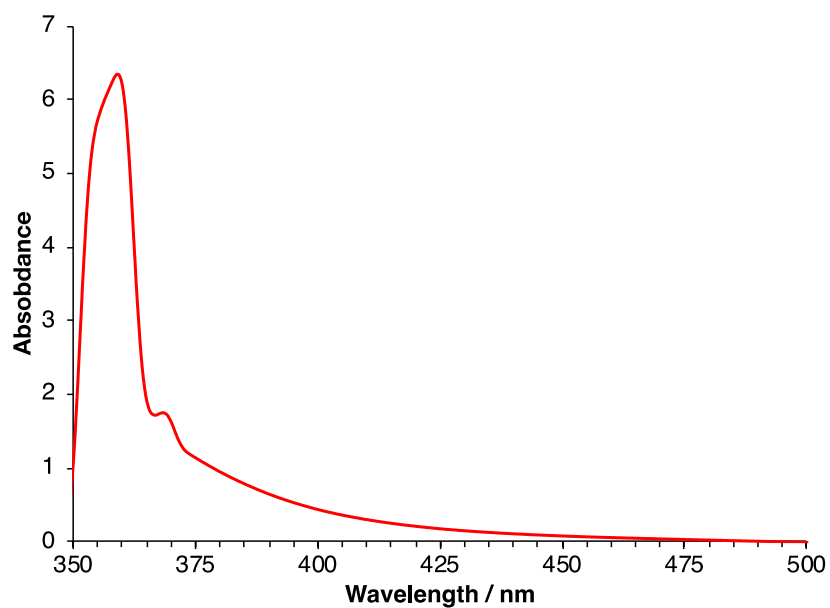


Figure S5. Differential UV/vis spectrum in Et_2O .

4. Crystallographic data

Table S1. Crystal data and structural refinement data for **1** and **5**.

Compound	1	5
Formula	C ₅₆ H ₈₀ Ge	C ₂₈ H ₄₀ Cl ₂ Ge
Molecular Weight	825.79	520.09
Temperature / °C	−180	−170
λ (Å)	0.71073	0.71075
Crystal size / mm ³	0.10 x 0.10 x 0.08	0.20 x 0.10 x 0.01
Crystal system	tetragonal	orthorhombic
Space group	<i>P</i> 4 ₁ (#76)	<i>P</i> 2 ₁ 2 ₁ 2 ₁ (#19)
<i>a</i> / Å	11.0197(1)	12.3031(2)
<i>b</i> / Å	11.0197(1)	13.7729(2)
<i>c</i> / Å	39.7580(7)	16.2300(3)
α / °	90	90
β / °	90	90
γ / °	90	90
<i>V</i> / Å ³	4827.96(12)	2750.16(8)
<i>Z</i>	4	4
μ / mm ^{−1}	0.669	1.321
<i>D</i> _{calcd.} / g·cm ^{−3}	1.136	1.256
θ_{max}	26.483	26.495
Refl./restr./param.	9991/1/563	5655/0/323
Completeness	99.8	99.1
GOF	1.123	1.137
<i>R</i> ₁ (<i>I</i> > 2σ(<i>I</i>))	0.0542	0.0291
w <i>R</i> ₂ (<i>I</i> > 2σ(<i>I</i>))	0.1239	0.0691
<i>R</i> ₁ (all data)	0.0628	0.0297
w <i>R</i> ₂ (all data)	0.1276	0.0696
Largest diff. peak and hole / e·Å ^{−3}	1.595, −0.492	0.358, −0.305
CCDC number	2106926	2106927

5. References

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